

Docket No. 2004P01759

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.	: 10/589,158	Confirmation No. 6958
Filing Date	: June 7, 2007	
Applicant	: Martin Seemann, et al.	
Title	: Process for the Synthetic Generation of Methane	
TC/AU	: 1795	
Examiner	: Imran Akram	
Docket No.	: 2004P01759	
Customer No.	: 24131	

DECLARATION UNDER 37 CFR § 1.132 IN SUPPORT OF
NON-OBVIOUSNESS

I, Serge Biollaz, do hereby declare the following:

1. I hold a Doctorate of Technical Science from the *Eidgenössische Technische Hochschule Zürich* (ETH Zurich) which is the Swiss Federal Institute of Technology in Zurich, Switzerland, granted in 1997.
2. I am currently head of the Thermal Process Engineering Group at the Paul-Scherrer Institute in Villigen, Switzerland .
3. I am an author or co-author of the following representative sample of peer reviewed articles:

J. Kopyscinski, T.J. Schildhauer and S.M.A. Biollaz, *Production of synthetic natural gas (SNG) from coal and dry biomass - A technology review from 1950 to 2009* , Fuel 89 (8), 1763 - 1783 (2010)

M.C. Seemann, T.J. Schildhauer, S.M.A. Biollaz, *Fluidised bed methanation of wood-derived producer gas for the production of*

Synthetic Natural Gas, Manuscript accepted for publication in Industrial & Engineering Chemistry Research (2010)

S.M.A. Biollaz, T.J. Schildhauer, D. Ulrich, H. Tremmel, R. Rauch, M. Koch, *Status Report of the Demonstration of BioSNG Production on a 1 MW Scale in Güssing*, 17th European Biomass Conference and Exhibition, Hamburg, Germany, 29 June - 3 July, (2009)

S.M.A. Biollaz, T.J. Schildhauer, M. Seemann, D. Ulrich, R. Rauch, *Successful demonstration of long term catalyst stability in the methane from wood process*, 16th European Biomass Conference in Valencia, 2-6 June (2008)

4. My research over the past 13 plus years has included, among other disciplines, research in biomass gasification, gas cleaning, and process chain analysis.
5. I am familiar with the disclosure, subject matter, and currently pending claims of US Patent Application No. 10/589,158 (the '158 application) of which I am a named co-inventor.
6. I currently have significant responsibility regarding the research and development of chemical processes, including research regarding the methane generation that is the subject of the '158 application.
7. The aforementioned responsibility for research and development of chemical processes, includes research regarding the methane generation that is the subject of the '158 application and includes evaluation of research and assistance in the preparation of patent applications.
8. Based on the facts and Exhibits set forth below, it is my professional opinion that the claims of the '158 application represent a novel process that is not present in any patent or scientific literature.
9. I have reviewed US Patent Nos. 3,928,000 (issued to Child); 3,912,775 (issued to Broeker); and 3,838,994 (issued to Aldridge) cited in the Office Action mailed by the United States Patent Office April 14, 2010 in the subject '158 patent application.

10. I have reviewed the Office Action mailed by the United States Patent Office on April 14, 2010 in the subject '158 patent application and the grounds set forth for rejecting the current claims.
11. I was personally involved in performing experiments according to the claimed invention at our experimental plant located in Guessing, Austria. The measurements have been conducted by the co inventors and myself, for a maximal non-stop operation of 200 hours. The table 1 below shows a set of results which were achieved with the experimental installation described in the original specification, starting with page 5, line 27. In the table, the measured gas concentrations and the calculated key figures are shown for each of the three phases Phase 1, 2 and 3 after a plant operation time of 200 hours for each of the three phases.

	Phase I		Phase II		Phase III	
[mol-%]	IN	OUT	IN	OUT	IN	OUT
H ₂	38.4	5.2	38.5	7.1	38.6	8.5
CO	28.9	0.3	25.8	1.0	26.4	0.5
CO ₂	18.3	47.7	19.9	46.2	20.1	46.4
CH ₄	11.6	44.1	10.8	42.2	10.3	42.1
C ₂ H ₂	0.3	0.0	0.4	0.0	0.4	0.0
C ₂ H ₄	1.1	0.0	2.6	0.0	2.7	0.0
C ₂ H ₆	0.0	0.0	0.1	0.3	0.1	0.4
N ₂	1.3	2.7	2.0	3.3	1.4	2.1
tars						
[mg/Nm ³]	IN	OUT	IN	OUT	IN	OUT
benzene	232	3	11806	142	13652	147
toluene	19	0	452	8	563	9
naphthalene	28	3	341	2	759	2
higher tars	16	0	374	0	488	0
U _{CO}	0.99		0.97		0.98	
U _{BTN}	-		0.990		0.992	
S _{CH₄}	0.58		0.60		0.60	
η _{ch}	0.83		0.81		0.82	

Table 1: Results of experiments in Guessing using a slip stream of the FICFB gasifier

The results in table 1 illustrate that the content of aromatic hydrocarbons which are present in the feed gas mixture are even completely removed in the phases 2 and 3 although the activated carbon filter was removed from the gas feed line. In phase 1, a conversion rate for these aromatic hydrocarbons U_{BTN} (i.e. Benzene, Toluene, Naphtaline) can be calculated since the activated carbon filter removes these contents before they enter the methane generation unit COALA. In both phases 2 and 3, the conversion rates U_{BTN} are equal or even larger than 99%. At the same time, the content of unsaturated C_2 components (C_2H_2 , C_2H_4) is removed completely from the feed gas mixture without deploying a negative impact on the selectivity of the fluidized bed catalyst. Both contents of aromatic hydrocarbons and unsaturated C_2 components are usually known to person skilled in the art as components which tarnish the selectivity of the catalytic material due to the formation of thin carbon/soot/tar layers on the catalytic material. This tarnishing process has been surprisingly absent under the conditions set out in the present invention even during the phases 2 and 3 maintaining the level of the conversion rate for methane S_{CH_4} at least at the same level as under phase 1. In particular, a slight increase of the conversion rate for methane has been observed which corresponds to the content of the aromatic hydrocarbons which contribute positively to the methane generation.

Summarizing the experimental results, it has to be pointed out that the process according to the new claim 1 delivers both a sustainable and stable conversion of harmful aromatic hydrocarbons and an endurable and stable generation of methane although an activated carbon filter is absent upstream of the fluidized bed reactor. This result is the

surprising teaching of the present invention which turns out to be operational on a long-term scale with a lower input of both fresh activated carbon (which is completely absent) and fresh catalyst material.

Child et al. (U.S. Pat No. 3,928,000) discloses a methanization process where the raw gas is originating from coal or coke under very specific conditions with respect to the removal of carbon monoxide. The raw gas generated from coal does contain usually a significant amount of sulphur components but does not contain higher hydrocarbons and aromatic hydrocarbon as compared to the feed gas mixture given in feature a) of the new claim 1. In addition, the teaching according to Child does not comprise the use of a fluidized bed catalyst as given in the feature b) of the amended claim 1.

Broeker et al. (US 3,912,775) discloses a process for the generation of methane using feedstocks as disclosed in column 4, lines 29 to 36, and in column 11, lines 60 to 66. These feedstocks are specific for the steam reforming process and rich gas process. In this point, the examiner fails to cope with the present claim language since the feedstock of Broeker et al. for this steam cracking of hydrocarbons consists to 100% of mixtures of hydrocarbons of average C number from C₁ to C₃₀, predominantly paraffinic hydrocarbons, but also aromatic hydrocarbons and naphthenic hydrocarbons. Therefore, the feedstock of Broeker is completely different from the feedstock used in our invention according to feature a) of the amended claim 1. The rich gases for the methanization of Broeker et al., i.e. mentioned in column 4, lines 41 to 54, from low temperature cracking of naphtha in general already contain, after drying, 50 to 75% methane, 19% to 25% of carbon dioxide, up to 16% of hydrogen and up to 5% of carbon monoxide. Broeker et al. further discloses that these gases now can pass over a nickel catalyst, using preheating temperatures from 200 to

300°C, without causing coking of the catalyst. At that stage, we have to point out that the feed gas of Broeker et al. which is passed to the methanization catalyst **is completely free** of C₂ components and aromatic hydrocarbons which is in contradiction to the composition of the feed gas according to the present invention.

In particular, the coking of the catalyst is already known by Broeker et al. when passing C₂ components and aromatic hydrocarbons over the methanization catalyst. Therefore, Broeker et al. has a two-stage process: Starting with the cracking of a feedstock that may comprise C₂ components and aromatic hydrocarbons to receive a feed gas for the subsequent methanization process that is completely free of any C₂ components and aromatic hydrocarbons and then the methanization step with this feed gas being completely free of C₂ components and aromatic hydrocarbons (see for example column 9, lines 43 to 46, column 10, lines 24 to 26, lines 47 to 51). To the contrary, in our invention, **C₂ and aromatic hydrocarbons must be present** in the composition of the feed gas used in the methanization step.

Therefore, even a combination of Child et al. and Broeker et al. can not lead to the present invention according to the amended claim 1 now presented. Both, Child et al. and Broeker et al. teach that the feed gas delivered to the methanization step is completely free of C₂ components and aromatic hydrocarbons. Broeker et al. only teaches the use of a feedstock for the steam cracking of hydrocarbons consisting in example 8 (column 11, lines 61 to 63) of 88% by volume of paraffins, 10 percent by volume of naphthenes with 6-membered rings and 2% by volume of aromatics. The composition of this feedstock has absolutely nothing in common with the composition of

the feed gas we use in the methanization step as claimed in claim 1, feature a).

Further, Aldridge (US 3,838,994) does not really know to handle an amount of C₂ to C₄ normally gaseous hydrocarbons and a minor amount of normally liquid hydrocarbons which are predominantly aromatics, such as benzene and toluene. According to the disclosure of Aldridge, the methanization process is carried out at an average temperature between 1000° and 1500°F (537° and 816°C). According to feature c) of our amended claim 1, our temperature ranges from 250 to 500°C which is clearly below the range of Aldridge. Obviously, these disadvantageous conditions of Aldridge are responsible for the undesirable C₂+ content Aldridge received for all of his product gases (see column 6, line 67, column 7, line 53, column 8, line 34, column 9, line 20). According to the measurements when working along the present invention, the C₂ components and aromatic hydrocarbons are completely consumed during the methanization step which is in fact a little bit surprising when considering that Aldridge still has C₂+ components in the product gas although using higher temperatures.

In fact, this is the very specific property of the present invention that a point/range of operation has been invented that overcomes the drawbacks of all prior art references.

12. Based on my review, and the distinctions set forth above, I do not believe that it would be obvious to a person of ordinary skill and knowledge in the art to combine the disclosures of Child and Broeker with Aldridge and reach the subject invention as now claimed.

Application No. 10/589,158
Declaration under 37 CFR 1.132

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-reference application or any patent issuing thereon.

Dr. Serge Biollaz

Date:_____